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(54) Title: THERMOSETTING RESIN COMPOSITIONS USEFUL AS UNDERFILL SEALANTS (57) Abstract The present invention provides a thermosetting resin composition useful as an underfilling sealant composition which (1) is capable of shrinking when cured, (2) rapidly fills the underfill space in a semiconductor device, such as a flip chip assembly which includes a semiconductor chip mounted on a carrier substrate, (3) enables the semiconductor to be securely connected to a circuit board by short-time heat curing and with good productivity, and (4) demonstrates excellent heat shock properties (or thermal cycle properties). The thermosetting resin compositions of this invention which are used as underfill sealants between such a semiconductor device and a circuit board to which the semiconductor device is electrically connected, include broadly (a) an epoxy resin component; (b) a (meth)acrylate resin component; (c) an inorganic filler component; and (d) a polymerization catalytic component.		

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THERMOSETTING RESIN COMPOSITIONS
USEFUL AS UNDERFILL SEALANTS

5

BACKGROUND OF THE INVENTION

Field of the Invention

This invention relates to thermosetting resin compositions useful as underfill sealants for mounting on a circuit board a semiconductor chip on a carrier substrate, particularly for those mounting steps involving flip chip ("FC") technology, and more particularly those mounting steps involving stud bump bonding ("SBB") technology.

Brief Description of Related Technology

15

In recent years, the increased popularity of smaller-sized microelectronic devices has made desirable size reduction of semiconductor devices. As a result, chip packages are becoming reduced in size to substantially that of the bare chip itself.

20

With size reduction has come an increasingly greater demand for large scale integration ("LSI") packaging technology to demonstrate enhanced density, performance and high processing capabilities.

In the past and even presently, chip packages were and continue to be connected to electrical conductors on a circuit board by use of solder connection or the like. However, when the resulting chip
5 package/circuit board structure is subjected to conditions of thermal cycling, reliability becomes suspect due to fatigue of the solder connection. In addition, while solder forms a continuous electrical contact path, the solder process involves first fluxing
10 and thereafter soldering. It would be desirable to eliminate a process step for time and economic reasons. Technological improvements have made conductive pastes a viable alternative to such solder connections.

Recent manufacturing advances provide a sealing
15 resin (often referred to as underfill sealant) in the space created by the mounting of a direct chip attachment ("DCA") [such as a chip scale package ("CSP")/ball grid array ("BGA") assembly] onto a circuit board to relieve stresses caused by thermal cycling. Underfill sealants
20 have been seen to improve heat shock properties and enhance the reliability of such structures.

Of course, curable resin compositions generally are known. For instance, Loctite Corporation presently offers for sale adhesive products intended to be useful
25 to bond a chip package to a circuit board (such as those products available under the trademark "CHIPBONDER", for instance, "CHIPBONDER" 348, 368, 3607 and the like) or as an underfill sealant (such as Loctite product No. 3150).

However, known resins oftentimes do not possess
30 all of the desired physical properties in either their uncured stage, post-cure stage or both, for certain commercial applications.

In connection with SBB processing technology, K. Amani et al., "MCM-ALIVH Using SBB Flip-Chip Bonding
35 Technique", 1997 Int'l Symp. Microelectronics, 278-83 (1997) and Y. Bessho et al., "Advanced Flip-Chip Bonding Technique to Organic Substrates", ISHM '95 Proc., 359-64 (1995) each report the use of an acid anhydride epoxy

underfill sealant in SBB FC assemblies. The purpose of this underfill sealant is stated in the Amani publication is to be "to enhance the structural stability and weather resistance of the bonded portion" (at 279) and in the
5 Bessho publication to "maintain compression force in the gap after curing, thus securing the stability of the bonding portions" (at 360). These purposes are quite common to underfill sealants generally.

An important parameter for many resin
10 compositions presently used as underfill sealants, particularly for SBB processing, in microelectronics applications is the contact resistance between the stud bump on the chip and the circuit board contacts. A high contact resistance may result in electrical
15 disconnection. Such an event is undesirable because it tends to cause intermittent operation of the microelectronic device, causing a failure of the device. The contact resistance itself tends to increase as the local operating temperature increases, and it may be
20 linked to the coefficient of thermal expansion of an underfill sealant.

It appears that an appropriate physical property of an underfill sealant in that regard would be shrinkage in volume after curing when a thermal
25 compression or lamination step has occurred during the microelectronic device fabrication process. Such a property is believed to reduce contact resistance.

While acrylate-based adhesives are known
generally to shrink in volume to some extent when cured,
30 such materials would typically be undesirable for microelectronic underfill applications because of their range of coefficients of thermal expansion when cured, which are ordinarily impractical for such applications.

Accordingly, it would be desirable to provide a
35 resin composition suitable for sealing the underfilling between a semiconductor chip and a circuit board, particularly where SBB technology is involved in the FC assembly process, which resin composition would possess

the ordinarily unwanted physical property of shrinking when cured. Such a physical property in this instance would aid in the compression interface of the stub bump of the chip and the contact points of the circuit board during assembly. To date, it is not believed that such a material is known for that purpose.

SUMMARY OF THE INVENTION

The present invention provides a thermosetting resin composition useful as an underfilling sealant composition which (1) is capable of shrinking when cured, (2) rapidly fills the underfill space in a semiconductor device, such as a FC assembly which includes a semiconductor chip mounted on a carrier substrate, (3) enables the semiconductor to be securely connected to a circuit board by short-time heat curing and with good productivity, and (4) demonstrates excellent heat shock properties (or thermal cycle properties).

The thermosetting resin compositions of this invention which are used as underfill sealants between such a semiconductor device and a circuit board to which the semiconductor device is electrically connected, include broadly (a) an epoxy resin component; (b) a (meth)acrylate resin component; (c) an inorganic filler component and (d) a polymerization catalytic component.

By using the thermosetting resin compositions of this invention, semiconductor devices, such as FC assemblies, may be (1) assembled, for instance using SBB techniques, rapidly and without production line down time because of improved cure speed and extended useful working life, and (2) securely connected to a circuit board by short-time heat curing of the composition, with the resulting mounted structure (at least in part due to the cured composition) demonstrating excellent heat shock properties (or thermal cycle properties).

The compositions of this invention may also be used for microelectronic applications beyond sealing underfill, such as with glob top, die attachment and

other applications for thermosetting compositions in which rapid cure time and an extended useful working life are desirable. The benefits and advantages of the present invention will become more readily apparent after a reading of the "Detailed Description of the Invention" together with the figure.

BRIEF DESCRIPTION OF THE DRAWING

FIG. 1 depicts a flow diagram of the assembly of a mounted structure in cross-sectional view with which the thermosetting resin composition of the present invention is used as an underfill sealant.

DETAILED DESCRIPTION OF THE INVENTION

As noted above, the thermosetting resin compositions which are useful as underfill sealants between a semiconductor device and a circuit board to which the semiconductor device is electrically connected, includes broadly (a) an epoxy resin component; (b) a (meth)acrylate resin component; (c) an inorganic filler component and (d) a polymerization catalytic component.

Typically, the composition includes of these components about 5 to about 25 parts of the epoxy resin component by weight of the total composition, about 15 to about 25 parts of the (meth)acrylate component by weight of the total composition, about 50 to about 70 parts of the inorganic filler component by weight of the total composition and about 0.01 to about 5 parts of the

polymerization catalytic component by weight of the total composition. Of course, depending on the particular set of properties desirable for a composition destined for a specific purpose these values may vary somewhat. Such variation may be achieved without undue experimentation by those persons skilled in the art, and accordingly are contemplated within the scope of the present invention.

The epoxy resin component of the present invention may include any common epoxy resin, such as a multifunctional epoxy resin. Ordinarily, the

multifunctional epoxy resin should be included in an amount within the range of about 20 parts to about 100 parts by weight of the total of the epoxy resin component. In the case of bisphenol-F-type epoxy resin, 5 desirably the amount thereof should be in the range of from about 1 to 40 parts, such as about 5 to about 30 parts by weight of the total of the epoxy resin component.

Examples of the multifunctional epoxy resin 10 include bisphenol-A-type epoxy resin, bisphenol-F-type epoxy resin (such as RE-404-S from Nippon Kayaku, Japan), phenol novolac-type epoxy resin, and cresol novolac-type epoxy resin.

Other suitable epoxy compounds include 15 polyepoxy compounds based on aromatic amines and epichlorohydrin, such as N,N,N',N'-tetraglycidyl-4,4'-diaminodiphenyl methane; N-diglycidyl-4-aminophenyl glycidyl ether;*and N,N,N',N'-tetraglycidyl-1,3-propylene 20 bis-4-aminobenzoate.

Among the epoxy resins suitable for use herein also include polyglycidyl derivatives of phenolic compounds, such as those available commercially under the tradename "EPON", such as "EPON" 828, "EPON" 1001, "EPON" 25 1009, and "EPON" 1031, from Shell Chemical Co.; DER 331, DER 332, DER 334, and DER 542 from Dow Chemical Co.; and BREN-S from Nippon Kayaku. Other suitable epoxy resins include polyepoxides prepared from polyols and the like and polyglycidyl derivatives of phenol-formaldehyde 30 novolacs, the latter of which are available commercially under the tradename "DEN", such as "DEN" 431, "DEN" 438, and "DEN" 439 from Dow Chemical. Cresol analogs are also available commercially under the tradename "ARALDITE", such as "ARALDITE" ECN 1235, "ARALDITE" ECN 1273, and 35 "ARALDITE" ECN 1299 from Ciba-Geigy Corporation, Hawthorne, New York. SU-8 is a bisphenol-A-type epoxy novolac available from Interez, Inc. Polyglycidyl adducts of amines, aminoalcohols and polycarboxylic acids

are also useful in this invention, commercially available resins of which include GLYAMINE 135, GLYAMINE 125, and GLYAMINE 115 from F.I.C. Corporation; ARALDITE MY-720, ARALDITE 0500, and ARALDITE 0510 from Ciba-Geigy and
5 PGA-X and PGA-C from the Sherwin-Williams Co.

Within the epoxy resin component should be an epoxy monomer capable of forming a high glass transition temperature polymeric network. Commercially available examples of such epoxy monomers are ERL-4221 from Union
10 Carbide Corporation, Danbury, Connecticut, and "ARALDITE" ECN-1871 from Ciba-Geigy.

And of course combinations of the different epoxy resins are also desirable for use herein.

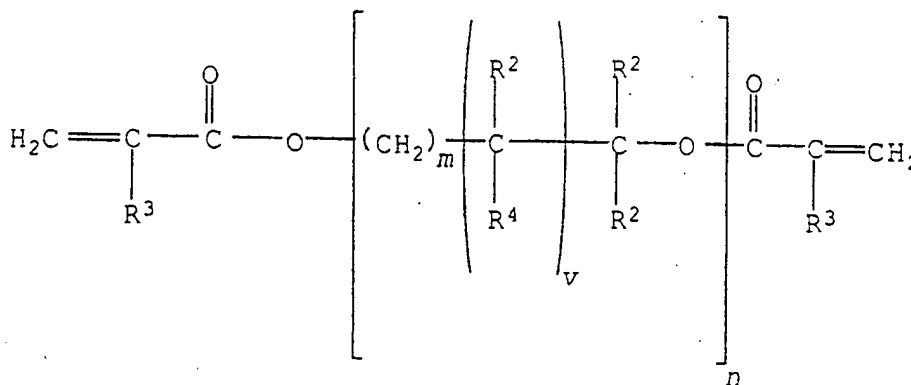
As the (meth)acrylate component of the
15 compositions of the present invention may be used a wide variety of (meth)acrylate monomers. For convenience, the term "(meth)acrylate" is intended to refer to both acrylate and methacrylate.

For instance, broadly (meth)acrylate monomers
20 suitable for use as the (meth)acrylate component in the present invention may be chosen from those represented by $H_2C=CGCO_2R^1$, where G may be hydrogen, halogen or alkyl groups having from 1 to about 4 carbon atoms, and R^1 may be selected from alkyl, cycloalkyl, alkenyl,
25 cycloalkenyl, alkaryl, aralkyl or aryl groups having from 1 to about 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with ~~silane, silicon, oxygen, halogen, carbonyl,~~
hydroxyl, ester, carboxylic acid, urea, urethane,
30 carbonate, amine, amide, sulfur, sulfonate, sulfone and the like.

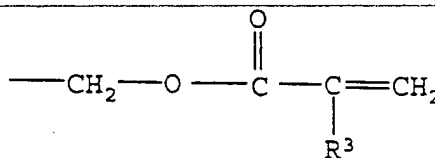
Additional (meth)acrylate monomers suitable for use herein include polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates,
35 hydroxypropyl (meth)acrylate ("HPMA"), hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate ("TMPTA"), diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol

di(meth)acrylate, dipropylene glycol di(meth)acrylate,
di-(pentamethylene glycol) di(meth)acrylate,
tetraethylene diglycol diacrylate, diglycerol
tetra(meth)acrylate, tetramethylene di(meth)acrylate,
5 ethylene di(meth)acrylate, neopentyl glycol diacrylate,
trimethylol propane triacrylate and bisphenol-A
di(meth)acrylates, such as ethoxylated bisphenol-A
(meth)acrylate ("EBIPMA").

Other (meth)acrylate monomers may also be used, such as reaction products of diglycidylether of bisphenol A with (meth)acrylic acid forming a (meth)acrylate ester corresponding to the structure shown below:

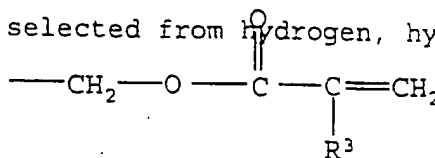


where R² may be selected from hydrogen, alkyl groups having from 1 to about 4 carbon atoms, hydroxyalkyl groups having from 1 to about 4 carbon atoms or



R³ may be selected from hydrogen, halogen, and alkyl groups of from 1 to about 4 carbon atoms;

R' may be selected from hydrogen, hydroxy and



m is an integer equal to at least 1, e.g., from 1 to about 8 or higher, for instance, from 1 to about 4;

v is 0 or 1; and

n is an integer equal to at least 1, e.g., 1 to
5 about 20 or more.

Higher-functionalized (meth)acrylates, such as penta, hexa, septa and the like, may also be used. Examples of such higher functionalized (meth)acrylates include pentaerythritol tetra(meth)acrylate,
10 dipentaerythritol penta(meth)acrylate, and polyester (meth)acrylates [e.g., tetra and hexa(meth)acrylate, commercially available examples of which include those sold by UCB Radcure, Inc., Smyrna, Georgia under the trademark "EBECRYL", such as "EBECRYL" 82 (low viscosity
15 modified polyester acrylate having fast cure and high glass transition properties), "EBECRYL" 450 (fast curing fatty acid-modified polyester hexaacrylate with excellent lithographic behavior and good pigment wetting), "EBECRYL" 657 (polyester tetraacrylate with excellent
20 lithographic behavior and pigment wetting for inks), "EBECRYL" 810 (fast curing multi-functional polyester acrylate with low viscosity), "EBECRYL" 830 (multi-functional polyester acrylate having fast cure, abrasion resistance, hardness and solvent resistance) and
25 "EBECRYL" 870 (hexafunctional polyester acrylate oligomer having good lithographic properties with fast cure)]

Urethane-functionalized (meth)acrylates may also be used herein. For instance, UCB offers for sale commercially a number of such materials including those
30 available under the trademark "EBECRYL", such as "EBECRYL" 264 [aliphatic urethane triacrylate diluted 15% with hexanediol di(meth)acrylate ("HDODA"), for providing non-yellowing, fast curing coatings with excellent
35 abrasion and stain resistance, toughness and flexibility], "EBECRYL" 265 [aliphatic urethane triacrylate diluted 25% with tripropylene glycol diacrylate ("TRGDA")], 1290

(hexafunctional aliphatic urethane acrylate containing an acrylated polyol diluent), "EBECRYL" 8301 (hexafunctional aliphatic urethane acrylate containing an acrylated polyol diluent, for providing fast cure with excellent hardness, solvent and abrasion resistance), "EBECRYL" 220 (multi-functional aromatic urethane acrylate containing an acrylated polyol diluent, which provides extremely fast cure with excellent hardness and solvent resistance properties), and "EBECRYL" 6602 (trifunctional aromatic urethane acrylate oligomer diluted to provide coatings with good hardness, scratch and abrasion resistance properties).

In addition, Sartomer Co., Exton, Pennsylvania offers sale commercially a number of such materials including CN 945 A60 (trifunctional urethane acrylate), CN 945 B85 (trifunctional urethane acrylate), CN 970 A60 (urethane acrylate), CN 970 E60 (urethane acrylate), CN 970 A80 (urethane acrylate), CN 972 (urethane acrylate), and CN 975 (hexafunctional urethane acrylate).

Of course, combinations of these (meth)acrylate monomers may also be used as the (meth)acrylate resin component of the present invention.

It is also within the scope of the invention for a material to be used as a component within either or both of the epoxy resin component and/or the (meth)acrylate component, which material is of a dual functionality (e.g., partially-acrylated epoxy resins). Examples of such materials include those which are

available from Sartomer under the trade designation SR-379, UCB under the trade designation "EBECRYL" 3605 and from Loctite Corporation, Rocky Hill, Connecticut under the trade designation EQM-672. As an inorganic filler component, many materials are potentially useful. For instance, the inorganic filler component may often include reinforcing silicas, such as fused silicas, and may be untreated or treated so as to alter the chemical nature of their surface. Virtually any reinforcing fused silica may be used.

Particularly desirable ones have a low ion concentration and are relatively small in particle size (e.g., on the order of about 2 microns), such as the silica commercially available from Admatechs, Japan under the trade designation SO-E5.

Other desirable materials for use as the inorganic filler component include those constructed of or containing aluminum oxide, silicon nitride, aluminum nitride and silica-coated aluminum nitride.

The polymerization catalytic component should include materials capable of catalyzing the polymerization of the epoxy resin component and the (meth)acrylate component portions, and any optional polymerizable components, of the inventive compositions. Of course, the materials included in the polymerization catalytic component are designed to catalyze polymerization of the composition, as a whole.

In order to catalyze polymerization of an epoxy resin as contemplated in the epoxy resin component, an imidizole would be an appropriate material to include. And polymerization catalysts with respect to the (meth)acrylate monomer as contemplated in the (meth)acrylate component may be achieved through the addition of peroxides, or other free radical generating materials, such as azo compounds [e.g., azo bis-isobutyronitrile (AIBN)]..

Of the about 0.01 to about 5 parts by weight of the polymerization catalytic component of the present invention, about 90 to about 50 percent thereof should be allocated to catalyze the polymerization of the epoxy resin component and about 10 to about 50 thereof should be allocated to catalyze polymerization of the (meth)acrylate component.

The imidizole component of the polymerization catalytic component may be chosen from imidizole, isoimidizole, and substituted imidizoles -- such as alkyl-substituted imidizoles (e.g., 2-methyl imidizole, 2-ethyl-4-methylimidizole, 2,4-dimethylimidizole,

- butylimidizole, 2-heptadecenyl-4-methylimidizole,
2-methylimidizole, 2-undecenylimidizole,
1-vinyl-2-methylimidizole, 2-n-heptadecylimidizole,
2-undecylimidizole, 2-heptadecylimidizole, 2-ethyl
5 4-methylimidizole, 1-benzyl-2-methylimidizole,
1-propyl-2-methylimidizole,
1-cyanoethyl-2-methylimidizole,
1-cyanoethyl-2-ethyl-4-methylimidizole,
1-cyanoethyl-2-undecylimidizole,
10 1-cyanoethyl-2-phenylimidizole,
1-guanaminoethyl-2-methylimidizole and addition products
of an imidizole and trimellitic acid,
2-n-heptadecyl-4-methylimidizole and the like, generally
where each alkyl substituent contains up to about 17
15 carbon atoms and desirably up to about 6 carbon atoms),
and aryl- substituted imidizoles (e.g., phenylimidazole,
benzylimidizole, 2-methyl-4,5-diphenylimidizole,
2,3,5-triphenylimidizole, 2-styrylimidizole, 1-(dodecyl
benzyl)-2-methylimidizole,
20 2-(2-hydroxyl-4-t-butylphenyl)-4,5-diphenylimidizole,
2-(2-methoxyphenyl)-4,5-diphenylimidizole,
2-(3-hydroxyphenyl)-4-,5-diphenylimidizole, 2-(p-dimethyla
minophenyl)-4,5-diphenylimidizole,
2-(2-hydroxyphenyl)-4,5-diphenylimidizole,
25 di(4,5-diphenyl-2-imidizole)-benzene-1,4,
2-napnthyl-4,5-diphenylimidizole,
1-benzyl-2-methylimidizole, 2-p-methoxystyrylimidizole,
and the like, generally where each aryl substituent
contains up to about 10 carbon atoms and desirably up to
30 about 8 carbon atoms.

Examples of commercial imidizoles are available
from Air Products, Allentown, Pennsylvania under the
trade designation "CUREZOL" 1B2MZ and from Synthron,
Inc., Morganton, North Carolina under the trade
35 designation "ACTIRON" NXJ-60.

Of course, combinations of these imidizoles are
also desirable for use in the polymerization catalytic
component of the compositions of the present invention.

Peroxides suitable for use in the polymerization catalytic component to catalyze the (meth)acrylate component of the compositions of this invention include t-butyl perbenzoate (commercially available from Elf Atochem, Philadelphia, Pennsylvania), dicumyl peroxide (commercially available from Aztec Peroxides, Inc., Houston, Texas under the trade designation DCP-R), hydroperoxides such as isopropyl cumene hydroperoxide (commercially available from Nippon Oils and Fats Co., Japan).

Additional components may also be used in the compositions of the present invention to achieve certain desired physical properties of the composition, the cured reaction product, or both.

For instance, the compositions may include a reactive co-monomer component for either or both of the epoxy resin and the (meth)acrylate monomer, such as a reactive diluent and/or an anhydride.

Appropriate reactive diluents for use herein may include monofunctional or certain multifunctional epoxy resins. The reactive diluent should have a viscosity which is lower than that of the epoxy resin component. Ordinarily, the reactive diluent should have a viscosity less than about 250 cps. In the event such a monofunctional epoxy resin is included as a reactive diluent, such resin should be employed in an amount of up to about 50 parts based on the total of the epoxy resin component.

The monofunctional epoxy resin should have an epoxy group with an alkyl group of about 6 to about 28 carbon atoms, examples of which include C₆-C₂₈ alkyl glycidyl ethers, C₆-C₂₈ fatty acid glycidyl esters and C₆-C₂₈ alkylphenol glycidyl ethers.

Commercially available monofunctional epoxy resin reactive diluents include those from Pacific Epoxy Polymers, Richmond, Michigan, under the trade designations PEP-6770 (glycidyl ester of neodecanoic acid), PEP-6740 (phenyl glycidyl ether) and PEP-6741

(butyl glycidyl ether).

Commercially available reactive diluents include those from Pacific Epoxy Polymers, under the trade designations PEP-6752 (trimethylolpropane
5 triglycidyl ether) and PEP-6760 (diglycidyl aniline).

Appropriate anhydrides for use herein include mono- and poly-anhydrides, such as hexahydrophthalic anhydride ("HHPA") and methyl hexahydrophthalic anhydride ("MHHPA") (commercially available from Lindau Chemicals,
10 Inc., Columbia, South Carolina, used individually or as a combination, which combination is available under the trade designation "LINDRIDE" 62C) and
5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1,2-dicar-

15 boxylic anhydride (commercially available from ChrisKev Co., Leewood, Kansas under the trade designation B-4400).

In addition, the composition may also include a flowability agent, such as a silane and/or titanate.

Appropriate silanes for use herein include
20 octyl trimethoxy silane (commercially available from OSI Specialities Co., Danbury, Connecticut under the trade designation A-137), glycidyl trimethoxysilane (commercially available from OSI under the trade designation A-187), methacryloxy propyl trimethoxy silane
25 (commercially available from OSI under the trade designation A-174).

Appropriate titanates for use herein include titanium IV tetrakis

30 [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0] [bis(ditridecylphosphito-0), dihydrogen], (commercially available from Kenrich Petrochemical Inc., Bayonne, New Jersey under the trade designation KR-55).

Optionally, the thermosetting resin composition of the present invention may further contain other
35 additives, such as defoaming agents, leveling agents, dyes, and pigments.

The thermosetting resin compositions of the present invention may be of the one-pack type, in which

all the ingredients are mixed together, or of the two-pack type in which the epoxy resin component, (meth)acrylate component, inorganic filler component, and other optional components are included in one part and
5 the polymerization catalytic component is stored separately in a second part, and mixed together only prior to use.

During application, the thermosetting resin compositions according to the present invention penetrate
10 and flow readily into the space between the semiconductor chip and the circuit board, or at least show a reduction in viscosity under heated or use conditions thus penetrating and flowing easily.

Generally, it is desirable to prepare
15 thermosetting resin compositions of this invention by selecting the types and proportions of the various components so that the gel times will be tailored to a specified period of time (such as 15 seconds, or 1 or 2 minutes) at a temperature of about 150°C. In such case,
20 the inventive compositions should show no or substantially no increase of viscosity after a period of time of about six hours. With such a gel time, the compositions penetrate into the space between the semiconductor chip and the circuit board (e.g., of 25 to
25 200 μm) relatively rapidly, and allow for a greater number of assemblies to be filled without observing a viscosity increase in the composition thereby rendering it less effective for application.

Reference to FIG. 1 shows a mounted structure
30 (i.e., a FC package prepared with SBB technology) in which a thermosetting resin composition of the present invention has been applied and cured.

The FC package 4 is formed by connecting a semiconductor chip (a bare chip) 2 to a carrier substrate
35 1 (e.g., a circuit board) and sealing the space therebetween suitably with a thermosetting resin composition 3.

More specifically, in the assembly of FC

semiconductor devices using SBB technology, the semiconductor chip 2 is passed over a substrate bearing a conductive adhesive paste (such as a metal-filled epoxy) to form a layer thereof on the studs 11 of the semiconductor chip 2. The layer is ordinarily formed by a printing mechanism. The conductive adhesive paste may be applied on either the carrier substrate or the semiconductor chip. Alternatively, this connection may also be made by an anisotropically conductive adhesive.

Thereafter, the semiconductor chip 2 is positioned over the carrier substrate 1 in such a manner so that the studs 11 (often made of gold) of the semiconductor chip 2 are in alignment with the bumps 12 (often made of gold or gold-plated copper) on the carrier substrate 1, which are now coated with a layer of conductive adhesive paste 10. The conductive adhesive paste may be cured by a variety of ways, though ordinarily a heat cure mechanism is employed.

In order to improve reliability, the space between the semiconductor chip 2 and the carrier substrate 1 is sealed with a thermosetting resin composition 3. The cured product of the thermosetting resin composition should completely fill that space.

Carrier substrates may be constructed from ceramic substrates of Al_2O_3 , SiN_3 , and mullite ($Al_2O_3-SiO_2$); substrates or tapes of heat-resistant resins, such as polyimides; glass-reinforced epoxy; ABS and phenolic substrates which are also used commonly as circuit

boards; and the like. Any electrical connection of the semiconductor chip to the carrier substrate may be used, such as connection by a high-melting solder or electrically (or anisotropically) conductive adhesive and the like. In order to facilitate connections, particularly in SBB technology, the electrodes may be formed as wire bond bumps.

After the semiconductor chip is electrically connected to the carrier substrate, the resulting structure is ordinarily subjected to a continuity test or

the like. After passing such test, the semiconductor chip may be fixed thereto with a thermosetting resin composition, as described below. In this way, in the event of a failure, the semiconductor chip may be removed
5 before it is fixed to the carrier substrate with the thermosetting resin composition.

Using a suitable application means, such as a dispenser, a thermosetting resin composition in accordance with this invention is applied to the
10 periphery of the electronically-connected semiconductor chip. The composition penetrates by capillary action into the space between the carrier substrate and the semiconductor chip.

The thermosetting resin composition is then
15 thermally cured by the application of heat. During the early stage of this heating, the thermosetting resin composition shows a significant reduction in viscosity and hence an increase in fluidity, so that it more easily penetrates into the space between the carrier substrate
20 and the semiconductor chip. Moreover, by preheating the carrier substrate, the thermosetting resin composition is allowed to penetrate fully into the entire space between the carrier substrate and the semiconductor chip.

Cured reaction products of the thermosetting
25 resin compositions of the present invention demonstrate excellent adhesive force, heat resistance and electric properties, and acceptable mechanical properties, such as flex-cracking resistance, chemical resistance, moisture
resistance and the like, for the applications for which
30 they are used herein.

The amount of thermosetting resin composition applied should be suitably adjusted so as to fill almost completely the space between the carrier substrate and the semiconductor chip, which amount of course may vary
35 depending on application.

Thermosetting resin compositions of the present invention may ordinarily be cured by heating to a temperature in the range of about 120 to about 180°C for

a period of time of about 0.5 to 30 minutes. However, generally after application of the composition, an initial cure time of about 1 minute sets up the composition, and complete cure is observed after about 10
5 to about 15 minutes at 165°C. Thus, the composition of the present invention can be used in relatively moderate temperatures and short-time curing conditions, and hence achieve very good productivity.

The present invention will be more readily
10 appreciated with reference to the examples which follow.

EXAMPLES

In these examples, compositions in accordance with the present invention were prepared and evaluated for performance.

15 Thermosetting resin compositions in accordance with the present invention were prepared by mixing together with stirring for a period of time of about 10 minutes at room temperature in an open vessel the following components in the order noted:

- 20 1. an epoxy resin component including
7.0 parts by weight of cycloaliphatic epoxy resin (commercially available from Union Carbide under the trade designation ERL-4221),
3.4 parts by weight of bisphenol-F-type
25 epoxy resin (commercially available from Nippon Kayaku under the trade designation RE-404-S), and
5.1 parts by weight of trimethyl propane
triglycidyl ether (commercially available from Pacific
Epoxy Polymers under the trade designation PEP-6752);
- 30 2. a (meth)acrylate component including
3.4 parts of TMPTA (commercially available from Sartomer under the trade designation SR-351);
3. an inorganic filler component including 65
parts of fused silica (commercially available from
35 Admatechs under the trade designation SO-E5); and
4. a polymerization catalytic component
including

0.06 parts of imidazole (commercially available from Air Products under the trade designation "CUREZOL" 1B2MZ), and

5 0.03 parts of t-butyl perbenzoate (commercially available from Elf Atochem).

Further components of the composition include:

5. 15.4 parts of an anhydride component comprised of a mixture in an 85:15 ratio of "HHPA" and "MHHPA" anhydrides (commercially available from Lindau
10 under the trade designation "LINDRIDE" 62C), and a cycloaliphatic dianhydride (commercially available from ChrisKev under the trade designation B-4400);

6. a flowability agent including the combination of the following silanes: 0.27 parts of octyl
15 trimethoxy silane (commercially available from OSI under the trade designation A-137); and 0.27 parts of a titanate, titanium IV tetrakis [2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0] [bis(ditridecylphosphito-0), dihydrogen], (commercially
20 available from Kenrich Petrochemical under the trade designation KR-55); and

7. 0.1 parts of a red pigment.

Four other formulations were prepared having the following components in the amounts noted below in
25 Table 1.

Table 1

Component	Identity	Sample No./Amount (wt%)			
		2	3	4	5
Epoxy resin	ERL-4221	5.5	4.72	5.6	7.5
	RE-404-S	3.1	2.65	3.1	1.5
(Meth)acrylate	TMPTA	6.2	5.25	6.2	4.5
Inorganic filler	SO-E5 (Silica)	65	70	65	65
Polymerization catalytic component	t-Butyl Perbenzoate (Peroxide)	0.07	0.04	0.02	0.05
	1B2MZ (Imidazole)	0.07	0.06	0.04	0.05
Reactive diluent -- epoxide	PEP-6752	5.5	4.72	5.5	4.74
Reactive diluent -- anhydrides	LINDRIDE 62C	12	10.3	12	--
	Methyl-Nadic Anhydride	--	--	--	12.8
	B-4400	2.1	1.8	2.15	2.2
Flowability agent	A-137 (Silane)	0.1	0.12	0.1	0.1
	A-187 (Silane)	0.1	0.12	0.1	0.1
	KR-55 (Titanate)	0.1	0.12	0.1	0.1
Pigment	Red Pigment	0.1	0.1	0.1	0.1

The compositions have a variety of properties in both the uncured and cured state which are measurable and useful parameters for the end user in choosing a particular formulation for a desired need.

For instance, in the uncured state, the flow rate and viscosity are of interest; in reaching the cured state, the reaction exotherm, as well as peak temperature and onset temperature are of interest.

The flow rate allows the end user to determine the rapidity with which the adhesive may be applied

during a fabrication process, such as a circuit assembly operation. It may be measured by passing the composition through a 25 μm gap between glass slides aligned perpendicular to one another, using metal shims as spacers. The time required for the composition to flow between the slides is then measured at lengths of about 0.25 to 1 inches. Values in seconds for the flow rates of the compositions set forth above are presented as an average of three measurements below in Table 2.

Table 2

Sample No.	Distance traveled			
	0.25"	0.50"	0.75"	1"
1	6	24	53	87
2	5	22	48	85

The value to which reference is ordinarily made is the time necessary to flow 0.5", in this case about 22 to about 24 seconds.

The viscosity is a property related to the flow rate, and is helpful for the end user in making appropriate decisions with respect to a particular formulation for a desired application. Viscosity here is measured using a Brookfield viscometer.

The reaction exotherm, or enthalpy, assists in determining the effectiveness of a (co)polymerization reaction. The reaction exotherm here is measured by differential scanning calorimetry ("DSC").

The peak temperature (" T_{PEAK} ") and onset

temperature (" T_{ONSET} ") may be determined from the DSC measurement. These values provide information for minimum reasonable curing temperatures, the curing temperature range, maximum reaction temperatures, and relative curing time at each temperature. See below Table 3.

Table 3

Sample No.	Property			
	Visc. (cps)	Enthalpy (J/g)	T _{PEAK}	T _{ONSET}
1	27,500	98	172	129
2	12,400	107	171	124

While the composition was used upon formation, it may be stored for a period of time of up to about 3 to about 6 months at a temperature of about -40°C without experiencing viscosity increase.

After formation, the composition was transferred to a 10 ml syringe made of non-reactive plastic.

When used, the composition may be dispensed through a 12G needle connected to the syringe into the junction between the carrier substrate and semiconductor chip in a previously-formed assembly. As such, the composition acts as an encapsulant for the electrical connection.

After such dispensing, the assembly was transferred to an oven while the temperature was maintained at about 165°C. The composition cured initially after about 1 minute, and thereafter cured completely after about 15 minutes at that temperature.

In the cured state, a variety of properties are useful depending on the end use for which the composition is destined.

For instance, the glass transition temperature ("Tg"), which is measured by DSC and by thermal mechanical analysis ("TMA"), provides information on the hardness and strength of the cured reaction product (or, network), and its behavior with respect to changes in temperature -- that is, a higher Tg should afford a material that is better able to withstand elevated temperatures. In addition, the coefficient of thermal expansion ("CTE"), which is also measured by TMA, provides information on the expectation of adherence of the cured reaction product to the substrates between

which the composition is dispensed as the temperature changes. Two CTEs are measured: one is measured below the Tg [CTE (α_1)] and the other is measured above the Tg [CTE (α_2)]. For instance, the CTE of a composition
5 destined for use with a chip and circuit board, should be about 30 ppm/°C or about 30 $\mu\text{m}/\text{m}^\circ\text{C}$, below the Tg. See below Table 4.

Table 4

Sample No.	Property			
	Tg -- DSC (°C)	Tg -- TMA (°C)	CTE (α_1) (ppm/°C)	CTE (α_2) (ppm/°C)
1	140	141	33	81
2	136	123	28-34	71.1
3	134	133	23-27	56-60
4	130	128	29	77
5	--	119	30-36	67-69

With respect to shelf-life stability, Sample
10 No. 5 was observed to experience a slow viscosity increase at room temperature. After a period of time of 5 hours, the viscosity increase was observed to be about 12%.

These formulations are presented as
15 illustrative, rather than limiting, examples of the inventive compositions. Many additional embodiments thereof are included in the spirit and scope of the invention.

What Is Claimed Is:

1. A thermosetting resin composition capable of shrinking when cured for sealing underfilling between a semiconductor device and a circuit board to which said semiconductor device is electrically connected, said composition comprising:
- (a) an epoxy resin component;
 - (b) a (meth)acrylate resin component;
 - (c) an inorganic filler component; and
 - (d) a polymerization catalytic component.
2. The composition according to Claim 1, further comprising a reactive co-monomer component.
3. The composition according to Claim 2, wherein the reactive co-monomer component is a member selected from the group consisting of reactive diluents, anhydrides and combinations thereof.
4. The composition according to Claim 3, wherein reactive diluent includes monofunctional epoxy resins selected from the group consisting of C₆-C₂₈ alkyl glycidyl ethers, C₆-C₂₈ fatty acid glycidyl esters and C₆-C₂₈ alkylphenol glycidyl ethers, glycidyl esters of neodecanoic acid, phenyl glycidyl ether, butyl glycidyl ether, trimethylolpropane triglycidyl ether, diglycidyl aniline, and combinations thereof.
5. The composition according to Claim 3, wherein the anhydride is selected from the group consisting of hexahydrophthalic anhydride, methyl hexahydrophthalic anhydride, 5-(2,5-dioxotetrahydrol)-3-methyl-3-cyclohexene-1, 2-dicarboxylic anhydride, and combinations thereof.
6. The composition according to Claim 1, further comprising a flowability agent.

7. The composition according to Claim 6,
wherein the flowability agent is a member selected from
the group consisting of silanes, titanates and
combinations thereof, wherein the silanes include
5 octyltrimethoxy silane, glycidyl trimethoxysilane, and
methacryloxy propyl trimethoxy silane, and the titanates
include titanium IV tetrakis
[2,2-bis[(2-propenyloxy)methyl]-1-butanolato-0]
[bis(ditridecylphosphito-0), dihydrogen]₂.

10 8. The composition according to Claim 1,
wherein the epoxy resin component includes a
multifunctional epoxy resin selected from the group
consisting of bisphenol-A-type epoxy resin,
bisphenol-F-type epoxy resin, phenol novolac-type epoxy
15 resin, cresol novolac-type epoxy resin, polyepoxy
compounds based on aromatic amines and epichlorohydrin,
polyglycidyl derivatives of phenolic compounds,
polyglycidyl derivatives of phenol-formaldehyde novolacs,
bisphenol-A-type epoxy novolac, polyglycidyl adducts of
20 amines, aminoalcohols, polycarboxylic acids and
combinations thereof.

9. The composition according to Claim 1,
wherein the epoxy resin component includes an epoxy
monomer capable of forming a high glass transition
25 temperature polymeric network.

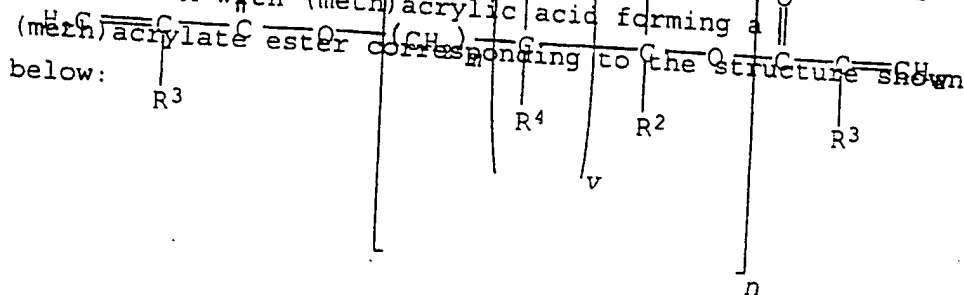
10. The composition according to Claim 1,
wherein the epoxy resin component is present in an amount
within the range of about 5 parts to about 25 parts by
weight of the total composition.

30 11. The composition according to Claim 1,
wherein the epoxy resin component includes a
multifunctional epoxy resin in an amount within the range
of about 20 parts to about 100 parts by weight of the

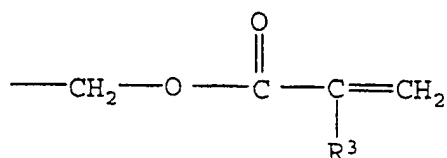
total of the epoxy resin component.

12. The composition according to Claim 1, wherein the (meth)acrylate resin component includes those within the following structure: $H_2C=CGCO_2R^1$, wherein G may be hydrogen, halogen or alkyl groups having from 1 to about 4 carbon atoms, and R^1 may be selected from alkyl, cycloalkyl, alkenyl, cycloalkenyl, alkaryl, aralkyl or aryl groups having from 1 to about 16 carbon atoms, any of which may be optionally substituted or interrupted as the case may be with silane, silicon, oxygen, halogen, carbonyl, hydroxyl, ester, carboxylic acid, urea, urethane, carbonate, amine, amide, sulfur, sulfonate and sulfone.

13. The composition according to Claim 1, wherein the (meth)acrylate resin component is selected from the group consisting of polyethylene glycol di(meth)acrylates, tetrahydrofuran (meth)acrylates and di(meth)acrylates, hydroxypropyl (meth)acrylate, hexanediol di(meth)acrylate, trimethylol propane tri(meth)acrylate, diethylene glycol di(meth)acrylate, triethylene glycol di(meth)acrylate, tetraethylene glycol di(meth)acrylate, dipropylene glycol di(meth)acrylate, di-(pentamethylene glycol) di(meth)acrylate, tetraethylene diglycol diacrylate, diglycerol tetra(meth)acrylate, tetramethylene di(meth)acrylate, ethylene di(meth)acrylate, neopentyl glycol diacrylate, trimethylol propane triacrylate bisphenol-A di(meth)acrylates, ethoxylated bisphenol-A (meth)acrylate, reaction products of diglycidylether of bisphenol A with (meth)acrylic acid forming a (meth)acrylate ester corresponding to the structure shown below:

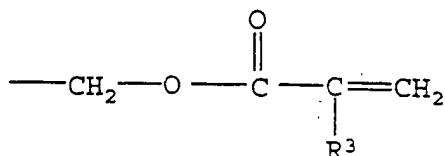


wherein R² may be selected from hydrogen, alkyl groups having from 1 to about 4 carbon atoms, hydroxyalkyl groups having from 1 to about 4 carbon atoms or



R³ may be selected from hydrogen, halogen, and alkyl groups of from 1 to about 4 carbon atoms;

R⁴ may be selected from hydrogen, hydroxy and



m is an integer equal to at least 1, e.g., from 1 to about 8 or higher, for instance, from 1 to about 4;

v is 0 or 1; and

n is an integer equal to at least 1, e.g., 1 to about 20 or more, and combinations thereof.

14. The composition according to Claim 1, wherein the (meth)acrylate component includes a member selected from the group consisting of pentaerythritol tetra(meth)acrylate, dipentaerythritol penta(meth)acrylate, polyester (meth)acrylates, tetra and hexa(meth)acrylate, low viscosity modified polyester acrylates, fatty acid-modified polyester hexaacrylates, polyester tetraacrylates, multi-functional polyester acrylates, hexafunctional polyester acrylate oligomers,

and combinations thereof.

15. The composition according to Claim 1,
wherein the (meth)acrylate component includes
urethane-functionalized (meth)acrylates selected from the
5 group consisting of aliphatic urethane triacrylate,
aliphatic urethane triacrylate, hexafunctional aliphatic
urethane acrylate, multi-functional aromatic urethane
acrylates, trifunctional aromatic urethane acrylate
oligomer, trifunctional urethane acrylates, urethane
10 acrylate, hexafunctional urethane acrylates and
combinations thereof.

16. The composition according to Claim 1,
wherein the epoxy resin component and the (meth)acrylate
resin component include partially (meth)acrylated epoxy
15 resins.

17. The composition according to Claim 1,
wherein the (meth)acrylate resin component is present in
an amount of about 15 to about 25 parts by weight of the
total composition.

20 18. The composition according to Claim 1,
wherein the inorganic filler component is selected from
the group consisting of organic filler component,
reinforcing silicas, fused silicas, aluminum oxide,
silicon nitride, aluminum nitride, silica-coated aluminum
25 ~~nitride, and combinations thereof.~~

19. The composition according to Claim 1,
wherein the inorganic filler component is present in an
amount of about 50 to about 70 parts by weight of the
total composition.

30 20. The composition according to Claim 1,
wherein polymerization catalytic component is capable of
catalyzing the polymerization of the epoxy resin

component and the (meth)acrylate component.

21. The composition according to Claim 1,
wherein polymerization catalytic component includes an
imidazole component for the epoxy resin component and a
5 free radical generating material for the (meth)acrylate
resin component.

22. The composition according to Claim 21,
wherein the imidazole component is a member selected from
the group consisting of imidazole, isoimidazole,
10 alkyl-substituted imidazoles, aryl-substituted
imidazoles, and combinations thereof.

23. The composition according to Claim 21,
wherein the free radical generating material is a member
15 selected from the group consisting of peroxides and azo
compounds, wherein the peroxides include perbenzoate,
dicumyl peroxide, isopropyl cumene hydroperoxide, and
combinations thereof, and the azo compounds include azo
bis-isobutyronitrile.

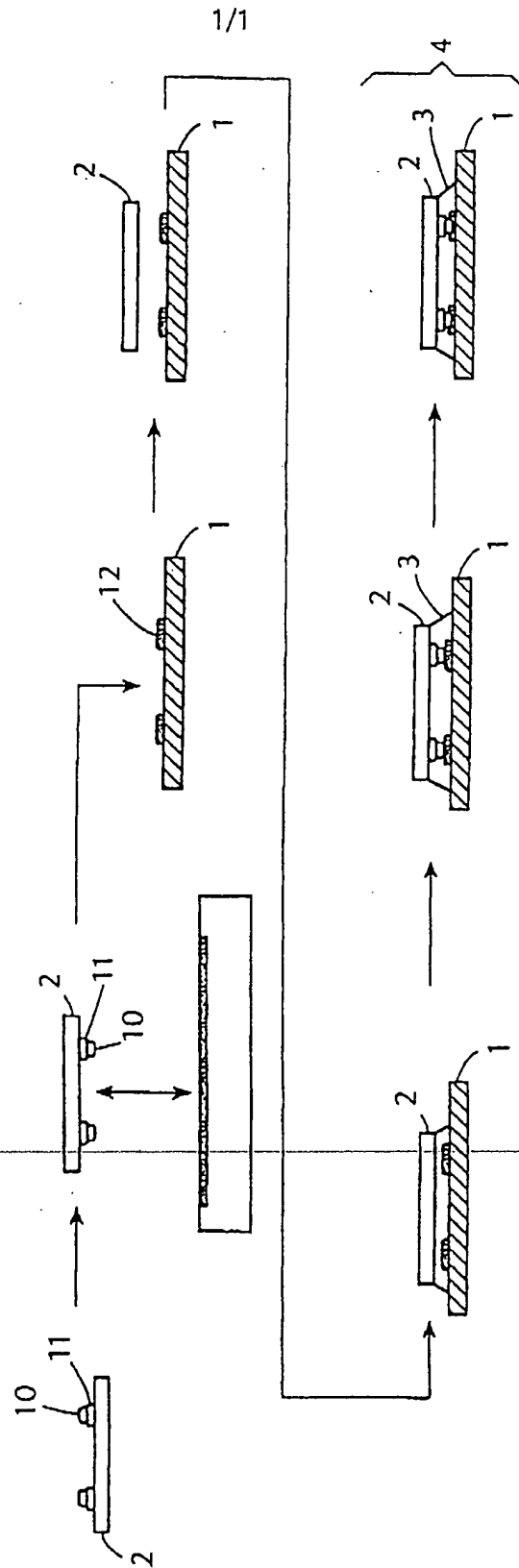
24. The composition according to Claim 1,
wherein the polymerization catalytic component is present
in an amount of about 0.01 to about 5 parts by weight of
the total composition.

25. The composition according to Claim 24,
25 wherein about 90 to about 50 percent of the
polymerization catalytic component catalyzes the
polymerization of the epoxy resin component and about 10
to about 50 percent of the polymerization catalytic
component catalyzes polymerization of the (meth)acrylate
30 component.

26. Reaction products formed from the
compositions according to any one of Claims 1 through 25.

27. An electronic device comprising a semiconductor device and a circuit board to which said semiconductor device is electrically connected assembled using a thermosetting resin composition according to any
5 one of Claims 1 through 25 as an underfill sealant between the semiconductor device and the circuit board, wherein the composition is capable of shrinking when cured.

FIG. 1



INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/13625

A. CLASSIFICATION OF SUBJECT MATTER IPC(6) : C08K 5/15, 5/101, 3/36, 3/22, 3/28; C08L 33/10, 33/12 US CL : 523/400, 524/430, 437, 443, 492, 502 According to International Patent Classification (IPC) or to both national classification and IPC		
B. FIELDS SEARCHED Minimum documentation searched (classification system followed by classification symbols) U.S. : 523/400, 524/430, 437, 443, 492, 502 Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched Electronic data base consulted during the international search (name of data base and, where practicable, search terms used) Please See Extra Sheet.		
C. DOCUMENTS CONSIDERED TO BE RELEVANT		
Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	US 4,917,466 A (NAKAMURA et al.) 17 April 1990 (17/04/90)	1-27
Y	US 5,596,023 A (TSUBOTA et al.) 21 January 1997 (21/01/97), col. 4, lines 13, 21-27, 46-58, 60-61 and 65, col. 5, line 2	1-3, 6-14, 16-18, 20-26
Y,P	US 5,864,178 A (YAMADA et al.) 26 JANUARY 1999 (26/01/99) col. 21, line 66, col. 22, line 2, col. 46, lines 35-40	1, 8-11, 21-23
A,P	US 5,784,779 A (GRUENWALD et al.) 28 July 1998 (28/07/98)	1-27
A,P	US 5,784,197 A (FREY et al.) 21 July 1998 (21/07/98)	1-27

☒ Further documents are listed in the continuation of Box C. ☐ See patent family annex.

* Special categories of cited documents:	*T	later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
A document defining the general state of the art which is not considered to be of particular relevance	*X*	document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
E earlier document published on or after the international filing date	*Y*	document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
L document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)	*A*	document member of the same patent family
O document referring to an oral disclosure, use, exhibition or other means		
P document published prior to the international filing date but later than the priority date claimed		

Date of the actual completion of the international search
23 AUGUST 1999

Date of mailing of the international search report
13 SEP 1999

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INTERNATIONAL SEARCH REPORT

International application No.
PCT/US99/13625

C (Continuation). DOCUMENTS CONSIDERED TO BE RELEVANT

Category*	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
Y,P	US 5,898,041 A (YAMADA et al.) 27 April 1999 (27/04/99) col. 1, lines 50-52, 59-60, col. 2, 16-29, col. 5, lines 45-67, col. 6, lines 1-17, col. 16, line 60, col. 17, line 8	1-7, 12-20, 24-27

INTERNATIONAL SEARCH REPORT

International application No.

PCT/US99/13625

B. FIELDS SEARCHED

Electronic data bases consulted (Name of data base and where practicable terms used):

APS, STN/CAS

Search terms: epoxy, (meth)acrylate, underfill, sealing resins, glob top, die attachment, anhydride, silica, aluminum oxide, silicon nitride, aluminum nitride, glycidyl ether, semiconductor, chip, dual or hybrid cure, partially (meth)acrylated epoxy resin, imidazole